

REMARKS

Original Claim 1 has been replaced by new Claim 7 in order to clearly identify the novel catalyst obtained by the novel steps of the process by which it is prepared. Claim 7 avoids is restricted solely to the novel combination of steps which are necessary to achieve a monoclinic zirconium dioxide catalyst or carrier which is substantially if not completely free of the tetragonal modification. This novel monoclinic zirconium dioxide requires a specific method of preparation but is also distinguished by surprisingly improved physical properties which have been specifically covered by new dependent Claims 8-10.

New Claims 11-14 have been added for the process itself in order to protect certain preferred features or variants of the process which lead to the best results. All of the new claims as well as amendments to the original claims are fully supported by the original disclosure. The most preferred catalyst is that from which the tetragonal modification of zirconium dioxide is practically undetectable in the final molded catalyst. However, applicants' also seek reasonable protection of the initially prepared catalyst or carrier which may still contain small amounts of the tetragonal modification which may then be later removed after the moldings have been produced, i.e. as part of a final calcination step. The claims are thus intended to protect both intermediate and final products of the overall process.

The original Claims 1 - 6 were rejected over the Bailar textbook reference (1973), pages 424-426, or the disclosure the Kortbeek et al '875 patent issued in 1984 (U.S. 4,440,875), the rejection being made under 35 USC 103 on the basis that applicants' novel process and the resulting process represent only an obvious variation of the cited art. It is admitted that applicants' procedure of adding the aqueous acidic solution of the zirconium salt to the basic water/ammonia mixture is directly opposite the procedure taught by Kortbeek '875 in which the ammonia is gradually added to a zirconiumoxychloride solution, as obtained by dissolving the oxychloride ($ZnOCl_2$) in water. There is no evidence to support the Examiner's bald conclusion that the order of addition of the of "the zirconyl chloride" and ammonia does not matter, The Examiner also errs in stating "...the same pH could be achieved by slow addition with mixing in any order".

Applicants' invention is not based on achieving a particular final pH of the solution but does require a gradual reduction in pH from the initial basic mixture of ammonia and water down to a final pH between 6 and 8, i.e. to complete the precipitation in the slightly acidic to slightly basic pH range of 6 to 8. Kortbeek '385 does just the opposite, starting from a slightly acidic solution of the zirconium-oxychloride and adding ammonia and completing this addition after reaching a neutral pH of 7 up to a strong basic pH of 10.

Applicants have identified prior art and have conducted comparative tests in their specification which clearly demonstrate that prior processes using different procedures for the precipitation invariably obtained a precipitated zirconium dioxide in which the content of the tetragonal modification was substantially greater than the monoclinic modification. (See Comparative Examples A - D on pages 6-7 of the present application.) Kortbeek '385 cannot be construed as "inherently" reducing the tetragonal modification of the zirconium dioxide to less than 15% while raising the monoclinic modification to 85% or more of the total zirconium dioxide content.

Evidence of "inherency" must be furnished by the prior art and not by stating that the prior art inherently obtain the same product because the prior art uses "substantially the same process". This line of reasoning begs the question when no proof of inherency is given. This is particularly true in the catalyst art where even slight changes in the procedures of preparing a catalyst often lead to new and unexpectedly improved catalytic properties. Based on their own experiments in the present application, applicants' can categorically state that their gradual reduction of the pH value does lead to surprising and unpredictable results in the structure and properties of the catalyst (or carrier) as well as providing a more effective and simpler process to produce a more than 85% content of the monoclinic zirconium chloride in the final catalyst.

The Examiner calls for a direct comparison of applicants' catalyst and its method of preparation with Kortbeek '385, but applicants' Comparative Example B is sufficiently close to Kortbeek in adding ammonia to up to a pH of 10.4 to show that such a procedure leads to about 80% of the tetragonal modification. A fair assessment of this evidence does establish unexpected and patentable results.

Both the new process Claims 11 - 14 and the original product-by-process Claims 1-6, now Claims 2 - 10, are essentially drawn to the same invention since it is not possible to completely separate the catalyst as a product from its essential method of preparation. However, the critical process step is that of the initial precipitation under a gradually decreasing pH value. An especially preferred process step is the substantially complete removal of any small residual amount of the tetragonal zirconium dioxide, especially in the preferred drying step of Claims 3 and 12. For the above reasons, favorable reconsideration and an allowance of all of Claims 2 - 14 are respectfully solicited.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "John H. Shurtleff".

Attorney for Applicants

John H. Shurtleff
Reg. No. 18,429
Tel: 312-236-5032
Chicago

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ENCLOSURE

(Replacing Claim 1)

--7. A catalyst or carrier consisting essentially of monoclinic zirconium dioxide which has been prepared by a process comprising the steps of initially precipitating a zirconium salt by adding a zirconyl nitrate or zirconyl chloride solution to an aqueous ammonia solution at a gradually decreasing pH of the initial ammonia solution down to a final pH value in the range of from 8 to not less than 6, and then subjecting the resulting precipitate to drying, calcining and molding steps to obtain a pelletized or other molded product.--

(New Claims)

AH --8. The product obtained by the process of Claim 1, wherein the dried and at least partly calcined monoclinic zirconium dioxide has a particle size of from 10 to 100 μm which is molded and optionally further calcined to reduce any tetragonal modification thereof to the detection limit of X-ray diffraction.--

--9. The product obtained by the process of Claim 1, wherein the final molded product has a BET surface area of from 60 to 150 m^2/g and a porosity of from 0.1 to 0.5 ml/g together with a pore distribution as determined by mercury porosimetry of two maxima at pore radii of about 70 AU and 4000 AU, the proportion of macropores having a pore radii above 1000 AU being from 20 to 50% of the total pore volume.--

--10. The product obtained by the process of Claim 1, wherein the abrasion value of the final molded product in the form of 3x3 mm pellets, after treatment for 2 hours with porcelain balls in a Vibratom vibratory mill at a frequency of 25 Hz, is from 1 to 10%.--

(New Process Claims)

--11. A process for the preparation of zirconium dioxide catalyst or carrier consisting essentially of at least 85 % by weight of the monoclinic modification of said zirconium dioxide and not more than 15% by weight of its tetragonal modification, which comprises:

preparing a concentrated aqueous acidic solution of a zirconium salt selected from the group consisting of zirconium chloride and zirconium nitrate;

adding this initially prepared solution gradually to a basic water/ammonia mixture at a temperature of about 20 to 60°C such that the pH value is slowly reduced from its initial upper limit of 14 until the addition is completed at a final pH value of from 8 down to not less than 6, the precipitate being recovered essentially free of ammonium salts, and

subsequently drying and calcining the recovered precipitate at temperatures of from 300 to 600°C and at pressures of from 0.5 to 5 bar.--

--12. A process as claimed in Claim 11, wherein any residual zirconium dioxide having the tetragonal modification is removed from the recovered precipitate prior to calcination by drying at an elevated temperature and under a water vapor partial pressure of from 0.2 to 0.9 bar.--

--13. A process as claimed in Claim 12, wherein the precipitated product or its molding is doped with sulfuric acid or a heteropolyacid to obtain a molded acidic catalyst or carrier.--

--14. A process as claimed in Claim 12, wherein the precipitated product or its molding is doped with a metal or metal salt solution as a catalyst component.--